Chem. Ber. **118**, 661 – 669 (1985)

Hydrated Oxocarbons, IV[1)]

Silylation of 1,1-Dihydroxy Compounds

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Received February 2, 1984

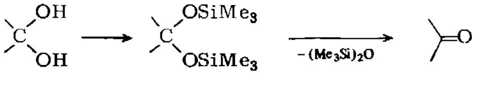
The action of various silylating agents on mono- and polyvicinal 1,1-dihydroxy compounds has been investigated. Some of these reagents converted ninhydrin (**2**) and rhodizonic acid (**17**) into the corresponding geminal bis(trimethylsilyloxy) derivatives **1** and **20**, respectively. Compound **1** readily fragments to form hexamethyldisiloxane and indantrione (**4**). The rhodizonic acid derivative **20** is, however, rather stable and even on pyrolysis at 500 °C gives only traces of the tetraketone **21**. With other silylating agents unexpected *C*-alkylation or *C*-amidation at the dihydroxy carbon is observed. Silylation of perhydroxycyclobutane and -cyclohexane leads to ring opened and contracted products.

Hydratisierte Oxokohlenwasserstoffe, IV[1)]

Silylierung von 1,1-Dihydroxy-Verbindungen

Die Anwendung von verschiedenen Silylierungsreagenzien auf mono- und polyvicinale 1,1-Dihydroxy-Verbindungen wurde untersucht. Mit einigen dieser Reagenzien konnten aus Ninhydrin (**2**) und Rhodizonsäure (**17**) die entsprechenden geminalen Bis(trimethylsilyloxy)-Derivate **1** und **20** gewonnen werden. Während **1** leicht zu Hexamethyldisiloxan und Indantrion (**4**) fragmentiert, ist **20** thermisch relativ stabil, es gibt pyrolytisch bei 500 °C nur Spuren des Tetraketons **21** ab. Andere Silylierungsreagenzien bewirken unerwartete *C*-Alkylierung oder *C*-Amidierung am Dihydroxykohlenstoff. Silylierungen von Perhydroxycyclobutan und -cyclohexan führen zu Ringaufspaltungs- bzw. Verengungsprodukten.

In the course of our efforts[2,3)] to arrive at the elusive neutral cyclic oxocarbons of the type $(CO)_n$ we now report our results on attempted "chemical" dehydration of appropriate *gem*-dihydroxy compounds using silylation and deoxysilylation by the sequence (1).



(1)

Results and Discussion

Applied to one of the simplest compounds of this class, ninhydrin (**2**), which can also be successfully dehydrated by heating in vacuo, chemically by the reaction with thionyl chloride[4)] or borylation-deoxyborylation[2)], we observed that the products formed

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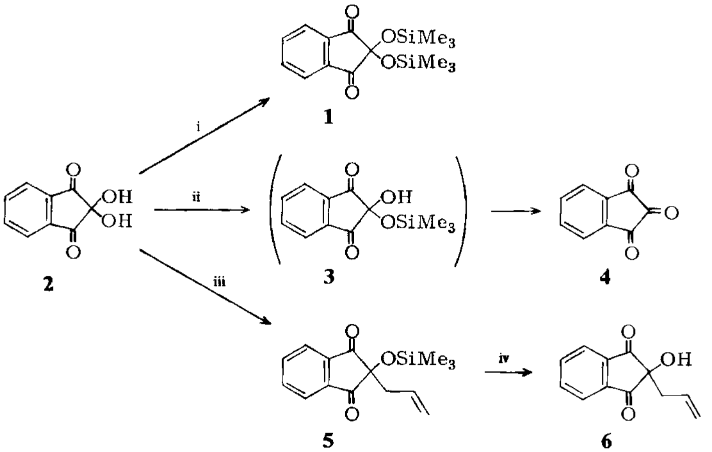
varied depending on the silylating agent used. Thus chlorotrimethylsilane in the presence of a tertiary amine smoothly and quantitatively dehydrates **2** to indantrione (**4**).

The bis(trimethylsilyloxy) derivative **1** of ninhydrin could be isolated from the reaction with allyltrimethylsilane as the main product, when trimethylsilyl triflate was used as catalyst and the reaction temperature was not allowed to rise above room temperature. When triflic acid is used as catalyst the product was, besides the *C*-allylated compound **5**[5], the trione **4** in 55% yield.

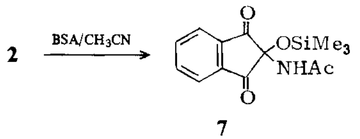
Scheme 1



i) $C_3H_5SiMe_3$, $CF_3SO_3SiMe_3$, MeCN, room temp.
ii) Me_3SiCl, Me_3N, Et_2O
iii) $C_3H_5SiMe_3$, CF_3SO_3H, MeCN
iv) MeOH

Compound **1** can be gas chromatographed at a column temperature of 150°C and be heated without noticeable decomposition up to its melting point at about 110°C. In solutions, however, it appears to be metastable and converts spontaneously to **4** on standing. It is therefore unlikely that **1** is an intermediate in the reactions where **4** is formed in situ. In these reactions the intermediacy of the hemiketal **3** is indicated. These reactions are summarized in Scheme 1.

When *O,N*-bis(trimethylsilyl)acetamide (BSA) is used as the silylating agent the reaction takes a different course and the amide derivative **7** is mainly formed.



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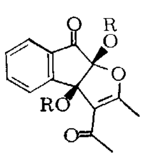
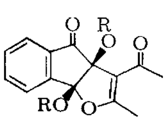
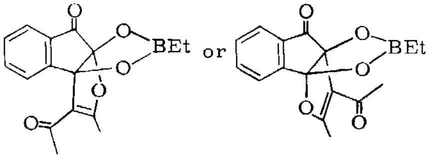
With the recently described trimethylsilyl enol ether of 2,4-pentanedione (Me_3Si-acac)[6], depending on the reaction conditions used, **2** forms one of the two isomeric *C*-alkylated products **8** (**8a**) or its *O,O'*-bis(trimethylsilyl) derivatives **9** (**9a**).



8: R = H
9: R = SiMe$_3$



8a: R = H
9a: R = SiMe$_3$



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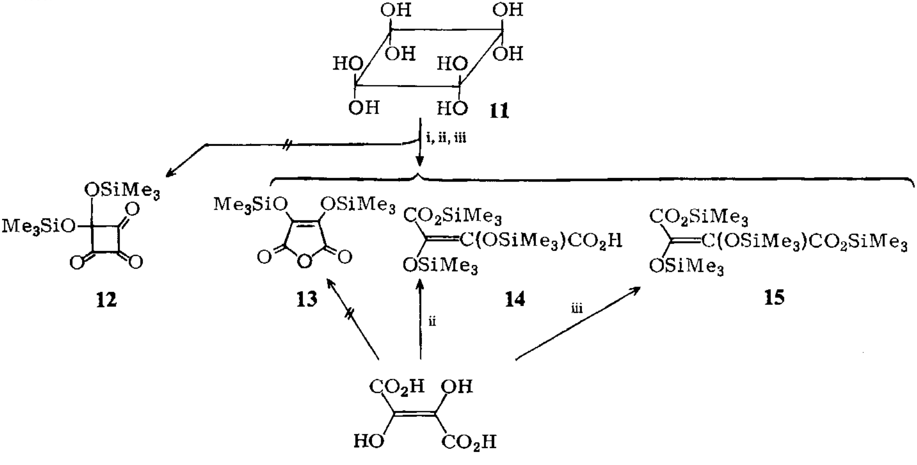
The *cis*-arrangement of the two hydroxyl groups in **8** was established by reacting the diol with triethylboroxine to give the dioxaborolane derivative **10**$^{7)}$.

The partial success of some of these silylating reagents in dehydrating ninhydrin to the trione **4** encouraged us to apply them to the dehydration of octahydroxycyclobutane (**11**).

All of the above silylating agents when reacted with **11** gave with variable yields mainly a product which initially was thought to be the trione **12**. It is a highly hygroscopic solid, melting at 25°C and boiling at 58 – 60°C/10^{-3} Torr. The elemental analysis and high resolution mass-spectroscopy established the elemental composition as $C_{10}H_{18}O_5Si_2$ (M^+: found *m/e* = 274.06872; calcd 274.06921). The fragmentation pattern was principally characterized by the loss of three CO's from the molecular ion to give a strong ion at *m/e* = 190 indicative of $(Me_3SiO)_2C^+$ ion. Furthermore, successive losses of one, followed by two CO's from the $M^+ - 15$ fragment gave the ions *m/e* = 231 and 175, respectively. The infrared spectrum showed bands at 1860, 1785 and 1695 cm^{-1}. The ^{1}H NMR spectrum showed only one signal at δ = 0.08, corresponding to the protons of the two chemically equivalent trimethylsilyl groups. In its ^{13}C NMR spectrum it showed two signals at δ = 162.64 and 134.12 and a quartet at δ = 0.61. While the MS, IR, and ^{1}H NMR spectra could well be accounted for by the trione **12**, the ^{13}C NMR spectrum does not agree with this structure. An *X*-ray crystallographic analysis$^{8)}$ showed it to be 2,3-bis(trimethylsilyloxy)maleic anhydride (**13**).

The formation of **13** was accompanied, depending on the reaction conditions used, by a host of other compounds as was evident from the GC-MS analysis of the product mixture. These included one with a molecular ion at *m/e* = 320 and two peaks showing molecular ions at *m/e* = 436. They could be separated from **13** by fractional crystallization and distillation, respectively. Their structures were ascertained by comparison with products of silylation of dihydroxyfumaric acid (**16**). In this reaction it was noted that when the silylation agent, Me$_3$Si-acac, was added directly to the solid **16**, and heated to about 70°C, an exothermic reaction followed by the evolution of about one equivalent of CO_2 gas resulted in the nearly quantitative formation of *Z*- or *E*-**14**$^{9)}$. The latter was identical to the *m/e* = 320 product above. When however, silylation is affected with allyltrimethylsilane, catalyzed by trimethylsilyl triflate in acetonitrile suspension of **16** and the reaction temperature is controlled at about 25°C, the expected persilylated product **15** is obtained quantitatively. The latter was found to be identical (by co-injection in GC) to one of the *m/e* = 436 peaks observed in the gas chromatogram of the product mixture from silylation of **11**. These reactions are shown in Scheme 2.

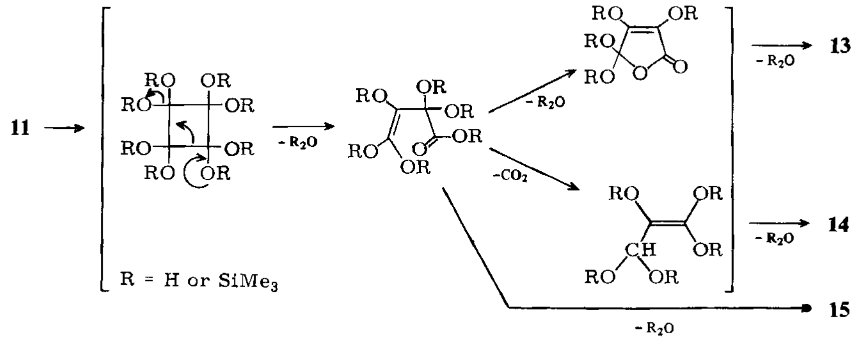
Scheme 2



i) Me_3SiCl, Me_3N, Et_2O
ii) Me_3Si-acac
iii) $C_3H_5SiMe_3$, $CF_3SO_3SiMe_3$, MeCN

As **13** was not observed in any of the silylation reactions of dihydroxyfumaric acid, the latter is unlikely to be initially formed in the ring opening process leading to the products observed. A reasonable pathway for the formation of these products is shown in Scheme 3.

Scheme 3

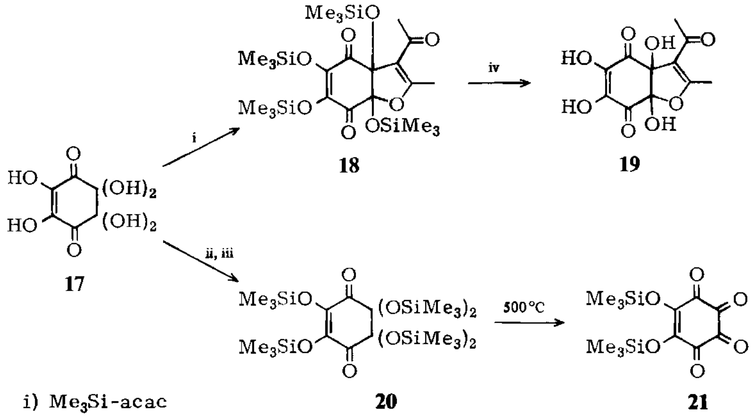


This tendency of **11** to undergo ring opening had previously been noted[2,3,10] and can be related to strain in the four-membered ring. It was therefore hoped to encounter a greater stability in the six-membered ring analogue of **11**.

Rhodizonic acid (**17**) with its only six hydroxyl groups can be regarded as a potential tetraketone and initially served as a model substrate. This compound has formally the bis(*gem*-dihydroxy) structure **17**[11]. Its silylation was expected to give the hexasilyloxy derivative **20** which either in situ or thermally should be convertible to the tetraketone **21**.

As in the case of ninhydrin the products depended on the silylating agent used. Thus, the reaction with Me_3Si-acac leads to C-alkylation with formation of **18**[12]. This reaction is analogous to the ninhydrin condensation product **9** and likewise can be smoothly desilylated in methanol to give **19**[12]. With allyltrimethylsilane in acetonitrile, catalyzed by triflic acid or less efficiently with BSA, it gives quantitatively the expected persilylated compound **20**. These reactions are shown in Scheme 4.

Scheme 4



i) Me_3Si-acac
ii) $C_3H_5SiMe_3$, CF_3SO_3H, MeCN
iii) BSA
iv) MeOH

Compound **20**, the structure of which has been established spectroscopically (^1H, ^{13}C NMR and MS), is surprisingly stable. It can be heated to its melting point at 239–240°C without any observable decomposition. Flash pyrolysis of **20** at 500°C resulted in a mixture. The MS analysis of the product indicated the presence of only a trace of the molecular ion corresponding to the tetraketone **21**. The major components appeared to be a number of ring-contracted products.

Unlike **17** which gave the persilylated derivative **20**, the silylation of perhydroxycyclohexane (**22**) gave directly a complex mixture of silylated ring-contracted products.

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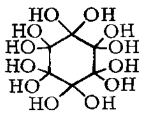

• 2 H_2O

It was shown that the method chosen, although successful in the dehydration of ninhydrin (**2**), is unsuited for the conversion of the more complex perhydroxycyclobutane and -cyclohexane to the target molecules. The mode of action of the silylating reagents used on these compounds is in many respects similar to their reactions in protic solvents and leads to ring-opened or -contracted products[13,14].

We are greatful to Dr. *U. Schubert* for providing us with the results of the *X*-ray analysis for compound **13**.

Experimental Part

Melting points: sealed capillary tubes, Büchi melting point apparatus, uncorrected. – ^{1}H NMR spectra: Varian EM 360 or Bruker WP 80. – ^{13}C NMR spectra: Varian XL 100. Internal standards (^{1}H, ^{13}C) tetramethylsilane. – Mass spectra: Varian CH 5.

Silylation of **2** *with Allyltrimethylsilane, Catalyzed with Trimethylsilyl Triflate. Formation of 2,2-Bis(trimethylsilyloxy)-1,3-indandione* (**1**): To a stirred suspension of 0.60 g (3.4 mmol) of ninhydrin in 50 ml of acetonitrile at room temperature was added dropwise a solution of 1.2 g (10 mmol) of allyltrimethylsilane and 0.1 ml of trimethylsilyl triflate in 5 ml of acetonitrile. After about 1 h the gas evolution ceased and the volatile compounds were removed at high vacuum. The residue was a straw coloured crystalline solid, m.p. 110°C (dec.), 1.1 g (100%). – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 7.9 (s, 4H); 0.05 (s, 18H). – MS: *m/e* = 322 (M^+, 30%); 307 (20); 294 (15); 265 (70); 147 (50); 73 (100).

Silylation of **2** *with Chlorotrimethylsilane. Formation of Indantrione* (**4**): A suspension of 0.43 g (2.4 mmol) of ninhydrin, 0.60 g (5.5 mmol) of chlorotrimethylsilane, and 0.4 ml (5.0 mmol) of pyridine in 10 ml of carbon tetrachloride was stirred at room temperature. The solid turned purple. After 3 h the solvent was evaporated and the residue subjected to high vacuum sublimation at 80°C to remove the pyridinium hydrochloride. The sublimation residue, a deep purple solid, weighed 0.38 g (99%), m.p. 254–255°C, and showed infrared spectrum identical to authentic **4**.

Silylation of **2** *with Allyltrimethylsilane, Catalyzed with Trifluoromethanesulfonic Acid:* To a stirred suspension of 1.0 g (5.6 mmol) of ninhydrin in 5 ml of acetonitrile at room temperature was added dropwise a solution of 1.6 g (14.0 mmol) of allyltrimethylsilane and 0.1 ml of triflic acid in 5 ml of acetonitrile. The solution turned deep purple and gradually a purple solid began to form. After about 1 h gas evolution ceased (total gas evolved 200 ml, calcd. 270 ml) and filtration gave 0.50 g (55%) of a deep purple solid, m.p. 254–255°C, identical to **4**. The filtrate on evaporation at high vacuum gave a viscous oil. It was dissolved in 5 ml of methanol and the solution left at room temperature over night. After removal of the volatile compounds the residue was separated by preparative TLC. The major fraction of *2-allyl-2-hydroxy-1,3-indandione* (**6**) weighed 0.20 g (18%), m.p. 66–67°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 8.01 (m, 2H); 7.93 (m, 2H); 5.71 (m, 1H); 5.15 (m, 2H); 2.78 (br. s, 1H); 2.56 (d of m, 2H). – MS: *m/e* = 202 (M^+, 18%); 160 (25); 132 (50); 105 (55); 104 (100).

$C_{12}H_{10}O_3$ (202.2) Calcd. C 71.28 H 4.98 Found C 71.02 H 4.78

Reaction of **2** *with O,N-Bis(trimethylsilyl)acetamide (BSA). Formation of 2-(Acetylamino)-2-(trimethylsilyloxy)-1,3-indandione* (**7**): A solution of 3 ml (12.1 mmol) of BSA in 5 ml of acetonitrile was added at 40°C to a stirred suspension of 1.0 g (5.6 mmol) of ninhydrin in 5 ml of acetonitrile. The mixture was stirred for 2 h. Initially the supernatant solution turned purple, but after a short time changed to yellow brown and the solid dissolved. The volatile compounds were removed at high vacuum and the residue dissolved in 5 ml of ether and the solution was triturated with pentane. An oil separated which over night gave a light-yellow crystalline solid weighing 1.5 g (93%). Recrystallized from ether/pentane it melted at 156–157°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.98 (m, 2H); 7.90 (m, 2H); 6.48 (br, 1H); 1.88 (s, 3H); 0.04 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 195.9 (s); 170.0 (s); 138.9 (s); 136.3 (d); 123.8 (d); 80.5 (s); 21.4 (t); 1.1 (t). – MS: *m/e* = 291 (M^+, 15%); 249 (55); 234 (25); 221 (10); 192 (30); 73 (100); 43 (50).

$C_{14}H_{17}NO_4Si$ (291.4) Calcd. C 57.71 H 5.88 N 4.81 Found C 57.61 H 5.70 N 4.88

Reaction of **2** *with 2,4-Pentanedione Trimethylsilyl Enol Ether to Give 3-Acetyl-3a,8a-dihydro-3a,8a-dihydroxy-2-methyl-8H-indeno[2,1-b]furan-8-one* (**8**) *or 3-Acetyl-3a,8b-dihydro-3a,8b-di-*

hydroxy-2-methyl-4H-indeno[1,2-b]furan-4-one (**8a**): The silylating agent (8.0 g, 46.5 mmol) was added dropwise to 3.2 g (18.0 mmol) of stirred ninhydrin. The reaction vessel was throughout cooled to about 15°C. The solid dissolved and after about 1 h a heavy white powder separated. The stirring was continued over night. The solid was filtered and washed several times with pentane. Recrystallisation from tetrahydrofuran/pentane gave 4.0 g (85%), m.p. 165°C (dec.). – ^{1}H NMR (80 MHz, [D$_6$]DMSO): δ = 8.15 (br., 1H); 7.83 (m, 4H); 6.38 (br., 1H); 2.41 (s, 3H); 2.13 (s, 3H). – MS: *m/e* = 260 (M$^+$, 10%); 242 (35); 218 (12); 200 (10); 176 (20); 43 (100). $C_{14}H_{12}O_5$ (260.2) Calcd. C 64.62 H 4.65 Found C 64.31 H 4.23

Reaction of **2** *with 2,4-Pentanedione Trimethylsilyl Enol Ether. Formation of 3-Acetyl-3a,8a-dihydro-2-methyl-3a,8a-bis(trimethylsilyloxy)-8H-indeno[2,1-b]furan-8-one* (**9**) *or 3-Acetyl-3a,8b-dihydro-2-methyl-3a,8b-bis(trimethylsilyloxy)-4H-indeno[1,2-b]furan-4-one* (**9b**): Ninhydrin (0.50 g, 2.8 mmol) was stirred with 8.0 g (46.5 mmol) of the silylating reagent. The reaction was exothermic and initially the temperature rose to about 40°C. The solid dissolved after 1 h and the light-yellow solution was allowed to stand over night. All volatile substances were evaporated at high vacuum. The residue was distilled at high vacuum, b.p. 150–152°C/10^{-3} Torr. The distillate, a slightly yellow oil, about 0.90 g (80%), solidified on standing to a colourless solid, m.p. 111–112°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.8 (m, 3H); 7.65 (dd, 1H); 2.46 (s, 3H); 2.17 (s, 3H); 0.30 (s, 9H); 0.10 (s, 9H). – ^{13}C NMR ($CDCl_3$): δ = 199.5 (s); 196.6 (s); 167.9 (s); 148.1 (s); 136.3 (d); 133.9 (s); 130.9 (d); 124.5 (d); 123.4 (d); 114.6 (s); 109.5 (s); 89.2 (s); 30.0 (s); 15.6 (s); 1.7 (s); 1.6 (s). – MS: *m/e* = 404 (M$^+$, 10%); 389 (20); 362 (15); 347 (22); 332 (10); 147 (30); 73 (100); 43 (30).

$C_{20}H_{28}O_5Si_2$ (404.6) Calcd. C 59.37 H 6.97 Si 13.88 Found C 59.74 H 6.89 Si 13.68

Methanolysis of **9**: A solution of 0.50 g (1.2 mmol) of **9** in 10 ml of methanol containing 0.1 ml of boron trifluoride etherate was refluxed for 1 h. The solvent and the volatile compounds were evaporated to give 0.30 g (93%) of a colourless crystalline solid which was recrystallized from tetrahydrofuran/pentane, m.p. 165°C (dec.) Infrared identical to **8** (**8a**).

Reaction of **8** (**8a**) *with Triethylboroxine. Formation of 3-Acetyl-3a,8a-(ethylboranediyldioxy)-3a,8a-dihydro-2-methyl-8H-indeno[2,1-b]furan-8-one or 3-Acetyl-3a,8b-(ethylboranediyldioxy)-3a,8b-dihydro-2-methyl-4H-indeno[1,2-b]furan-4-one* (**10**): 0.21 g (0.81 mmol) of **8** (**8a**) and 0.35 ml (1.7 mmol) of triethylboroxine in 20 ml of toluene were heated to reflux. About 15 ml of toluene was removed by azeotropic distillation. The remainder of the volatile compounds was removed in vacuo, and the residue recrystallized from chloroform/pentane, m.p. 106–107°C. – ^{1}H NMR (60 MHz, CD_2Cl_2): δ = 7.8 (m, 4H); 2.45 (s, 3H); 2.19 (s, 3H); 0.90 (s, 5H). – MS: *m/e* = 298 (M$^+$, 75%); 256 (90); 241 (25); 238 (50); 43 (100).

Silylation of Octahydroxycyclobutane (**11**): A mixture of 2.0 g (10.9 mmol) of **11**, 15 g (138 mmol) of chlorotrimethylsilane and 6.0 g (100 mmol) of trimethylamine in 200 ml of ether was stirred at room temperature for 24 h. The solution was filtered and the ether evaporated at reduced pressure. The remaining slightly yellow oil was distilled at high vacuum. Two fractions boiling at 55–80 and 85–100°C were collected. The low boiling distillate when cooled to 0°C partially crystallized. Removal of the supernatant liquid gave 1.7 g of a colourless solid. Repeated distillation at 58–60°C/10^{-3} Torr gave 1.4 g of a sample which was 87% pure by GLC (20 m OV 101 capillary column) and which could be recrystallized from pentane at –30°C to give analytically pure *2,3-bis(trimethylsilyloxy)maleic anhydride* (**13**), m.p. about 25°C. – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 0.08 (s). – ^{13}C NMR ($CDCl_3$): δ = 162.64 (s); 134.12 (s); 0.61 (q). – IR (film): 1860, 1785, 1695 cm^{-1}. – Raman: 1869 m; 1778 m; 1700 s cm^{-1}. – MS: *m/e* = 274 (M$^+$, 4%); 259 (10); 231 (8); 190 (40); 175 (3); 147 (50); 73 (100).

$C_{10}H_{18}O_5Si_2$ (274.4) Calcd. C 43.77 H 6.61 Si 20.47 Found C 43.95 H 6.51 Si 20.63

The supernatant liquid of the lower boiling distillation fraction was purified by preparative GLC and found to be identical to the silylation product **14** of dihydroxyfumaric acid. The higher boiling fraction (102 – 110 °C) was analyzed by GC-MS (20 m OV 101 capillary column). It showed besides traces of **13** and **14** mainly two components (A 22 and B 64%, respectively), both with M^+ at *m/e* = 436. Component A was found by co-injection to be identical to the silylation product **15** of dihydroxyfumaric acid.

Silylation of 2,3-Dihydroxymaleic(fumaric) Acid (**16**) *with 2,4-Pentanedione Trimethylsilyl Enol Ether:* The silylating agent (Me_3Si-acac, 5.0 g, 29.1 mmol) was added dropwise to 1.0 g (6.7 mmol) of stirred, vacuum dried solid acid **16**. On completion of the addition the resulting solution was heated to about 70 °C for 1/2 h. Carbon dioxide (150 ml) evolved (calcd. 160 ml). The solution on evaporation of volatile substances at high vacuum was distilled, b.p. 55 – 60 °C/10^{-2} Torr. Yield 2.0 g (92%) of **14**. – ^1H NMR (60 MHz, $CDCl_3$): δ = 7.0 (s, 1 H); 0.26 (s, 9 H); 0.21 (s, 9 H); 0.15 (s, 9 H). – ^{13}C NMR ($CDCl_3$): δ = 166.0 (s); 138.0 (d, J_{CH} = 83 Hz); 129.5 (s); 0.2 (s); –0.2 (s); –0.6 (s). – MS: *m/e* 320 (M^+, 5%); 305 (60); 221 (35); 147 (65); 73 (100).

$C_{12}H_{28}O_4Si_3$ (320.6) Calcd. C 44.96 H 8.80 Si 26.28 Found C 45.23 H 8.83 Si 26.03

Silylation of 2,3-Dihydroxymaleic(fumaric) Acid (**16**) *with Allyltrimethylsilane. Formation of* **15**: A solution of 3.5 g (30.7 mmol) of allyltrimethylsilane and 0.1 ml of trimethylsilyl triflate in 5 ml of acetonitrile was added during 2 h to a stirred suspension of 0.82 g (5.5 mmol) of freshly dried **16** in 5 ml of acetonitrile at room temperature. A slightly exothermic reaction took place releasing propene gas. After about 3 h the gas evolution ceased and the volatile substances were evaporated at high vacuum at room temperature. The residue was distilled, b.p. 65 – 70 °C/10^{-3} Torr to give 2.3 g (95%) of **15**. – ^1H NMR (60 MHz, $CDCl_3$): δ = 0.32 (s, 18 H); 0.22 (s, 18 H). – MS: *m/e* = 436 (M^+, 8%); 421 (35); 319 (2); 147 (40); 73 (100).

Reaction of Rhodizonic Acid (**17**) *with 2,4-Pentanedione Trimethylsilyl Enol Ether:* A mixture of 1.0 g (4.8 mmol) of **17**-dihydrate and 6.1 g (35.5 mmol) of the silylating reagent in 30 ml of hexane was stirred for 48 h at room temperature. The slightly turbid solution was filtered and the volatile compounds were removed at high vacuum. The residue, a beige crystalline mass, was recrystallized from hexane at –78 °C. The resulting crystals of **18**[12], m.p. 150 °C (dec.), weighed 2.4 g (86%). – ^1H NMR (80 MHz, $CDCl_3$): δ = 2.3 (s, 3 H); 2.2 (s, 3 H); 0.35 (s, 18 H); 0.3 (s, 9 H); 0.1 (s, 9 H). – ^{13}C NMR ($CDCl_3$): δ = 195.7 (s); 189.9 (s); 185.7 (s); 168.1 (s); 147.3 (s); 145.7 (s); 115.6 (s); 102.9 (s); 87.0 (s); 29.5 (t); 15.4 (t); 1.8 (t); 1.3 (t); 0.8 (t); 0.6 (t). – MS: *m/e* 558 (M^+, 5%); 543 (10); 453 (20); 441 (5); 199 (15); 147 (18); 73 (100).

$C_{23}H_{42}O_8Si_4$ (588.9) Calcd. C 46.91 H 7.19 Si 19.08 Found C 46.59 H 6.93 Si 18.98

Methanolysis of **18**: A solution of 2.0 g (3.4 mmol) of **18** in 5 ml of methanol was left at room temperature over night. The colourless needles formed were filtered and recrystallized from a little methanol to give 0.75 g (82%) of **19**[12], m.p. 204 °C (dec.). – ^1H NMR (60 MHz, $[D_8]$THF): δ = 7.50 (br., 2 H); 2.30 (s, 3 H); 2.15 (s, 3 H). – MS: *m/e* = 270 (M^+, 2%); 228 (3); 224 (7); 168 (6); 85 (20); 43 (100).

$C_{11}H_{10}O_8$ (270.2) Calcd. C 48.90 H 3.73 Found C 48.70 H 4.00

Persilylation of Rhodizonic Acid (**17**). *Formation of 2,3-Dihydro-2,2,3,3,5,6-hexakis(trimethylsilyloxy)-1,4-benzoquinone* (**20**): To a stirred suspension of 1.0 g (4.8 mmol) of vacuum-dried **17**-dihydrate in 20 ml of acetonitrile was added 6.0 g (53 mmol) of allyltrimethylsilane and 0.1 ml of triflic acid. After about 3 h of stirring at room temperature the solution was complete and the gas evolution had ceased. The volatile substances were removed at high vacuum, and the residue gave a light-yellow crystalline solid. Recrystallized from pentane/ether it gave 3.0 g (97%)

of a colourless solid, m.p. 239 – 240°C (dec.). – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 0.35 (s, 18H); 0.20 (s, 36H). – ^{13}C NMR ($CDCl_3$): δ = 191.6 (s); 145.5 (s); 99.3 (s); 2.1 (s); 1.1 (s). – MS: *m/e* = 638 (M^+, 5%); 623 (15); 521 (75); 147 (35); 73 (100).

$C_{24}H_{54}O_8Si_6$ (639.2) Calcd. C 45.10 H 8.52 Si 26.36 Found C 45.25 H 8.16 Si 26.48

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8) *U. Schubert,* unpublished results.

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10) Octahydroxycyclobutane reacts with acetic anhydride at 150°C to give quantitatively diacetoxymaleic anhydride, *M. Yalpani,* unpublished results.

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